EFFECTS OF STORAGE TEMPERATURE AND STORAGE DURATION ON BIODIESEL PROPERTIES, VISUAL APPEARANCES, AND EMISSION

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ABSTRACT

Biofuels based on vegetable oils offer the advantage being a sustainable and environmentally attractive alternative to conventional petroleum based fuel. Biodiesel is produced from any fat or oil such as soybean oil, through a refinery process called transesterification. The key issue in using vegetable oil-based fuels is oxidation stability, stoichiometric point, bio-fuel composition, antioxidants on the degradation and much oxygen with comparing to diesel gas oil. Biodiesel can be used as a pure fuel or blended with petroleum in any percentage but the standard storage and handling procedures used for biodiesel are the main issue due to the biodiesel fuel specifications. In the quest for fulfill the industry specifications standard; the fuel should be stored in a clean, dry and dark environment. In this research, three different storage temperature were study which are; low (0 – 5 °C), ambient (25 – 29 °C), and high (40 – 50 °C). The key parameters that are required to store biodiesel are discussed, and the recent research advances are noted. Five types of biodiesel after storage all the samples for 2016 hours were tested plus with two product of combustion. Images analysis for combustion process was used to image appearances analysis. Under 2016 hours of storage duration, the effect of degradation was happen although the effect is not significance because the changes are still in acceptable ranges.

ABSTRAK

Bahan api biodiesel berasakan minyak sayuran menawarkan kelebihan menjadi bahan api yang mampan dan mesra alam yang menarik sebagai alternatif kepada bahan api berasaskan petroleum konvensional. Biodiesel yang dihasilkan daripada lemak atau minyak seperti minyak kacang soya, melalui proses penapisan yang dipanggil 'transesterification'. Isu utama dalam menggunakan bahan api berasaskan minyak sayur-sayuran ialah kestabilan pengoksidaan, titik stoikiometri, komposisi bahan api biodiesel, antioksidan terhadap penurunan kualiti dan kandungan oksigen yang tinggi dibandingkan gas minyak diesel. Biodiesel boleh digunakan sebagai bahan api tulen atau dicampur dengan peratusan petroleum, tetapi standad penyimpanan dan prosedur pengendalian yang digunakan untuk biodiesel adalah isu utama kerana spesifikasi bahan api biodiesel. Dalam usaha untuk memenuhi standard industri spesifikasi; minyak perlu disimpan dalam persekitaran yang bersih, kering dan gelap. Dalam kajian ini, tiga suhu penyimpanan yang berbeza dikaji iaitu; suhu rendah (0 - 5 °C), suhu persekitaran (25 – 29 °C) dan suhu tinggi (40 - 50 °C). Parameter utama yang diperlukan untuk menyimpan biodiesel dibincangkan, dan kemajuan penyelidikan yang baru dicatatkan. Lima jenis spesifikasi biodiesel selepas penyimpanan semua sampel untuk 2016 jam diuji ditambah dengan dua produk daripada pembakaran. Analisis imej untuk proses pembakaran digunakan untuk analisis imej penampilan Pada 2016 jam tempoh penyimpanan, kesan penurunan kualiti telah berlaku walaupun kesan tidak ketara kerana perubahan masih dalam julat yang boleh diterima.

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NOMENCLATURE

BHT	-	Butylatedhydroxyl tolune
BHA	-	Butylatedhydroxyl anisole
TBHQ	-	Ter-butyl hydroxyl quinone
GA	-	Gallic acid
PY	-	Pyrogallol
ASTM	-	American Society for Testing and Material
EN	-	European Standards
RPM	-	Revolution per minute
CO_2	-	Carbon dioxide
CO	-	Carbon monoxide
SO_2	-	Sulfur dioxide
NO_x	-	Nitrogen oxide
HC	-	Hydro carbon
PM	-	Particulate matter
Å	-	Angstrom is a unit of length equal to 10^{-10}m
ppm	-	part per million
mg KOH/g	-	milligram potassium hydroxide per gram
mm^2/s	-	square millimeter per second
kg/m^3	-	kilogram per cubic meter

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The global issue of climatic change and global warming is greatly influenced by green house effect. One of the major factors of greenhouse effect is an increase in the level of carbon dioxide. National Geographic Web Site (2010) has mention the carbon dioxide emission has increased steadily over years, causing the unstable weather conditions such as typhoons which become more frequent and fatal all across the globe. There are various sources like volcanic eruption, forest fire, and consumption of fossil fuel (petrol and diesel) releases carbon dioxide that causes greenhouse effect. The consumption and demand for the petroleum products are increasing every year due to increase in population, standard of living and urbanization. The increase in crude oil import affects the country's economy and its development.

The global energy concerns have led to the search for alternative energy source and to increase awareness on the environmental issues resulting from the extensive consumption of fossil fuels [1].

Biodiesel is one of the most promising alternative renewable energy options to substitute petroleum based diesel. Its primary advantages are that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. [2] It can also be used directly in most diesel engines without requiring extensive engine modifications.

1.2 Problem Statement

Biodiesel can be used as a pure fuel or blended with petroleum in any percentage but the standard storage and handling procedures used for biodiesel are the main issue due to the biodiesel fuel specifications. The fuel should be stored in a clean, dry, dark environment. Acceptable storage tank materials include aluminum, steel, fluorinated polyethylene, fluorinated polypropylene and teflon. Copper, brass, lead, tin, and zinc should be avoided. However, many technologies for reducing exhaust emissions of wide variety of biodiesel fuel engines have been considered with the improvement throughout the combustion process but small research measured the effects from the storage method.

Fuel-grade biodiesel must be produced to strict industry specifications (ASTM D6751 or EN 14214) in order to insure proper performance. The key issue in using vegetable oil-based fuels is oxidation stability, stoichiometric point, bio-fuel composition, antioxidants on the degradation and much oxygen with comparing to diesel gas oil.

Purpose of this study is to analyze the effect of storage method on the fuel properties. One of the examples in the effect of biodiesel properties is the reduction of kinematics viscosity. It would be able to improve NO_x and soluble organic fraction (SOF) emissions at low load and also can be reduced by using high squish combustion chamber which continues high turbulence combustion in the chamber.

The application of the biodiesel in the diesel engines offer not only attractive and more economical fuel but also creates problems of injector coking, dilution of engine oil, deposits in various parts of engine during extended operation of the engine and emissions problems. Biodiesel is a fuel comprising mono-alkyl esters of medium to long-chain fatty acids derived from vegetable oils or animal fats. Typically, engines operated on biodiesel exhibit higher emissions of oxides of nitrogen (NO_x) compared with petroleum diesel. The increase in NO_x emissions might be an inherent characteristic of cooking oil poly unsaturation, because the level of saturation is known to affect the bio diesel’s cetane number, which can affect NO_x.

1.3 Objectives

The objectives of this research are;

1. To investigate the effect of storage temperature and storage duration on fuel properties, visual appearances and emission
2. To suggest a suitable storage temperature and attempts the optimum fuel characteristics that predominantly influences to the high combustion efficiency, and emission reductions

1.4 Scope of the Project

The scope of study includes the following:

1. A study on the effect of storage method on the characteristic of biodiesel such as acid value, flash point, water content, density, and kinematic viscosity. This experimental study to validate the changes biodiesel properties.
2. A direct photography method will applied in this experiment. This technique of study is to investigate the relation between fuel properties and flame development that inflame to exhaust emission
3. Three several of storage temperature, low temperature: 0°C – 5°C, ambient temperature 25°C – 29°C, and high temperature: 40°C –50°C.
4. Duration storage is about 2016 hours.
5. Six different blended biodiesel B5, B10, B15, B25, B35, and B45 will compare with B100 biodiesel.
6. Product of combustion will be analyzed: ash and carbon monoxide (CO).
7. Transparent glass bottle used in this study with 1 liter storage capacity.

1.5 Significant of Study

This study is important to determine and suggest the best storage method and condition of biodiesel to get lowest degradation of biodiesel during storage period. The results are very important for future study and development as a reference to establish a new alternative energy that produced lower effects to our earth and further reduce dependence on fossil fuels. The optimum storage condition or temperature will suggested from this study to make sure the degradation of biodiesel under the minimum changes.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Burning fossil fuels such as coal, diesel and gas produces greenhouse gases give impacts on the environment. A range of greenhouse gases were produced when fossil fuels are burned, these gases include carbon dioxide, water vapour, methane and nitrous oxides. These gases trap the sun's heat in the Earth's atmosphere, thus, acting like a 'greenhouse'. These gases concentrate and increase the heat of the sun where it works quite similar to the lens in a magnifying glass. This is called the greenhouse effect.

The major cause of the enhanced greenhouse effect is burning fossil fuels. For the past 20 years, about three quarters of greenhouse gas emissions were caused by burning fossil fuels. Following the increase in greenhouse gases in our atmosphere, the Earth's climate is changing. This phenomenon is called climate change.

Studies have found that first-generation biofuels produced from current feedstock's using the most efficient systems and carbon releases results in emission reductions in the range of 20-60 per cent relative to fossil fuels. Generally, biofuels offer many priorities, including sustainability, reduction of greenhouse gas emissions, regional development, social structure and agriculture and security of supply [3].

On the other hand, biomass sources will be more attractive since the scarcity of conventional fossil fuels, growing emissions of combustion generated pollutants and their increasing costs [4]. Many people already have an interest in biomass use, in which it has the properties of being a biomass source and a carbon neutral source [5].

Biofuel has almost very close property to that of diesel fuel and is also renewable, biodegradable, non-toxic [6][7]. It can be produced from vegetable oil and animal fats. Oils or fats are basically triglycerides which are composed of three long-chain fatty acids [8][9]. These oils or triglycerides cannot be used as fuel because of high viscosity. In order to be used as fuel, viscosity has to be reduced, triglycerides are converted into esters by transesterification reaction [10]. Thus, three smaller molecules of ester and one molecule of glycerine are obtained from one molecule of fat or oil. Glycerine is then removed as by product and esters are known as biodiesel.

Current oil and gas reserves were suggested by experts that it would suffice to last only a few more decades. So, fuels such as biodiesel and bioethanol are in the forefront of the alternative technologies to exceed the rising energy demand and reducing petroleum reserves [10].

2.2 Biodiesel Overview

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100. A “mono-alkyl ester” is the product of the reaction of a straight chain alcohol, such as methanol or ethanol, with a fat or oil (triglyceride) to form glycerol (glycerin) and the esters of long chain fatty acids. Biodiesel can be used as B 100 (neat) or in a blend with petroleum diesel. A blend of 20 % biodiesel with 80 % petro diesel, by volume, is termed “B 20”. A blend of 2 % biodiesel with 98 % petro diesel is “B 2”, and so on [11].

Biodiesel is an alternative fuel for diesel engines that is receiving great attention worldwide as it reduces the dependence on petroleum products, the energy crisis, global climate changes and environmental pollution.

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propylorethyl) esters. Biodiesel is typically made by chemically reacting lipids (vegetable oil, animal fat) with an alcohol producing fatty acid esters or fatty acid methyl esters.

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petro diesel. Biodiesel can also be used as a low carbon alternative to heating oil.

Biodiesel and its blends can be used in diesel engines without any major modification. It is defined by ASTM that it is a fuel composed of Mono alkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats [12].

2.2.1 Feed Stocks of Biodiesel

Alternative diesel fuels produced from natural, renewable sources such as vegetable oil and fats. Soybean, sunflower, palm, rapeseed, canola, cotton seed and jatropha are the most commonly used oils for the production of biodiesel [8]. Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are considered in as potential low priced biodiesel sources. Meanwhile, beef, sheep tallow, poultry oil from animal sources and waste cooking oil are also sources of raw materials [13].

2.2.2 Basic Chemistry and Chemical Processing

The major components of vegetable oils are triglycerides. The term triacylglycerol (triglycerides) is being used more and more [11]. Triglycerides are esters of glycerol with long-chain acids, commonly called fatty acids. Tables 2.1 and 2.2, list the most common fatty acids and their corresponding methyl esters.

Table 2.1: Chemical structure of common fatty acids and methyl esters [11].

Fatty acid	Structure	Common Acronym	Methyl Ester
Palmitic acid / Hexadecanoic acid	$R-(CH_2)_{14}-CH_3$	C16:0	Methyl palmitate / hexadecanoate
Stearic acid / Octadecanoic acid	$R-(CH_2)_{16}-CH_3$	C18:0	Methyl stearate / octadecanoate
Oleic acid / 9 (z) - octadecanoic acid	$R-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$	C18:1	Methyl oleate / 9(z) - octadecanoate
Linoleic acid / 9 (z), 12 (z) - octadecanoic acid	$R-(CH_2)_7-CH=CH-CH_2-CH=CH-(CH_2)_4-CH_3$	C18:2	Methyl oleate / 9(z), 12(z) - octadecanoate
Linoleic acid / 9 (z), 12 (z), 15 (z) - octadecanoic acid	$R-(CH_2)_7-(CH=CH-CH_2)_3-CH_3$	C18:3	Methyl oleate / 9(z), 12(z), 15(z) - octadecanoate

R = COOH (CO_2H) or $COOCH_3$ (CO_2CH_3); $(CH_2)_7$ = $CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$, etc.

Table 2.2: Characteristics of common fatty acids and methyl esters [11]

Fatty acid (Methyl ester)	Formula	Molecular weight	Melting point (°C)
Palmitic acid Methyl palmitate	$C_{16}H_{32}O_2$ $C_{17}H_{34}O_2$	256.428 270.457	63-64 30.5
Stearic acid Methyl stearate	$C_{16}H_{32}O_2$ $C_{17}H_{34}O_2$	284.481 298.511	70 39
Oleic acid Methyl oleate	$C_{18}H_{34}O_2$ $C_{19}H_{36}O_2$	282.465 296.495	16 -20
Linoleic acid Methyl linoleate	$C_{18}H_{32}O_2$ $C_{19}H_{34}O_2$	280.450 294.479	-5 -35
Linolenic acid Methyl linolenate	$C_{18}H_{30}O_2$ $C_{19}H_{32}O_2$	280.450 294.479	-11 -52 / -57

The most important issue during biodiesel production is the completeness of the transesterification reaction. The basic chemical process that occurs during the reaction is indicated in Figure 2.1.

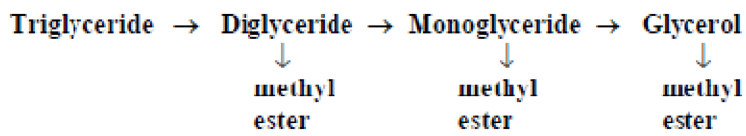

Figure 2.1: Completion of reaction in biodiesel process.

The triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of a methyl ester of a fatty acid. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released.

2.3 Milestones of Biodiesel

The key milestones in the development of biodiesel industry were shown in Table 2.3 [13]. In fact, the usage of vegetable oils in diesel engine could be dated back to August 10, 1893. On this day, Rudolf Diesel, the inventor of the diesel engine, ran on his prime engine model in Augsburg, Germany. The engine model has been fuelled nothing but peanut oil. In remembrance of this event, August 10 has been declared ‘‘International Biodiesel Day”. Dr. Diesel was visionary. Back in 1912, he has long predicated that usage of vegetable oils for engine fuels would one day become as important as petroleum and the coal–tar products of the present time.

This diesel engine continued to be used until the 1920s before fossil-based diesel almost completely eliminated vegetable oils in the market due to cheaper price, higher availability and government subsidies. The diesel engine was then modified to run on the lower viscosity petroleum fuel, now known as ‘‘diesel’’. Nevertheless, Diesel’s ideas on agriculture and his invention contributed to the foundation for a society with clean, renewable, locally grown fuel [14].

In 1970s, there was a shortage of fossil fuels supply and security had prompted new interest in developing vegetable oils as alternative energy. However, the altered diesel engine is no longer suitable for high viscosity and low volatility vegetable oils to be applied directly. Some operational problems were reported due to the high viscosity of vegetable oils compared to fossil-based diesel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Refinement has to be made in order to turn those vegetable oils into quality fuel. Attempts to overcome these problems included pyrolysis, blending [15][16] and micro emulsification [17]. Yet, problems were still found with carbon deposition and contamination [18]

Table 2.3: Key milestones in the development of biodiesel industry [13]

Date	**Event**
August 10, 1893	Rudolf Diesel's prime diesel engine model, which was fuelled by peanut oil, ran on its own power for the first time in Augsburg, Germany
1900	Rudolf Diesel showed his engine at the world exhibition in Paris, his engine was running on 100% peanut oil
August 31, 1937	A Belgian scientist, G. Chavane was granted a patent for a 'Procedure for the transformation of vegetable oils for their uses as fuel'. The concept of what is known as 'biodiesel' today was proposed for the first time
1977	A Brazilian scientist, Expedito Parente, applied for the first patent of the industrial process for biodiesel
1979	Research into the use of transesterified sunflower oil and refining it to diesel fuel standards was initiated in South Africa
1983	The process for producing fuel-quality, engine tested biodiesel was completed and published internationally
November, 1987	An Austrian company, Gaskoks established the first biodiesel pilot plant
April, 1989	Gaskoks established the first industrial-scale plant

1991	Austria's first biodiesel standard was issued
1997	A German standard, DIN 51606, was formalized
2002	ASTM D6751 was first published
October, 2003	A new Europe-wide biodiesel standard, EN 14214 was published
September, 2005	Minnesota became the first US state to mandate that diesel fuelled sold in the state contain part biodiesel requiring a content of at least 2% biodiesel
October, 2008	ASTM published new biodiesel blend specification standards
November, 2008	The current version of the European Standard 14214 was published and supersedes EN 14214:2003

Transesterification of a vegetable oil was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. The transesterification process converts vegetable oils to their alkyl esters and reduces the viscosity to diesel fuel level, producing biodiesel with properties similar to petroleum-based diesel fuel. Therefore, this process has become the most viable process to transform vegetable oils to be usable in existing engines.

The concept of what is known as ‘‘biodiesel” today was proposed for the first time when a Belgian scientist, G. Chavanne was granted a patent for a ‘‘Procedure for the transformation of vegetable oils for their uses as fuels” in 1937 [19]. Later, a Brazilian scientist, Expedito Parente, applied the first patent for biodiesel to be industrialised in 1977 [13]. Meanwhile, at South Africa, research for the production and refining of biodiesel using sunflower oil was initiated in 1979. By 1983, the process for producing fuel quality, engine-tested biodiesel was completed and published internationally [13]. An Austrian company, Gaskoks, obtained the technology from a South African Agricultural Engineers; subsequently established the first biodiesel pilot plant and the first industrial-scale plant in 1987 and 1989, respectively.

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